



CASE

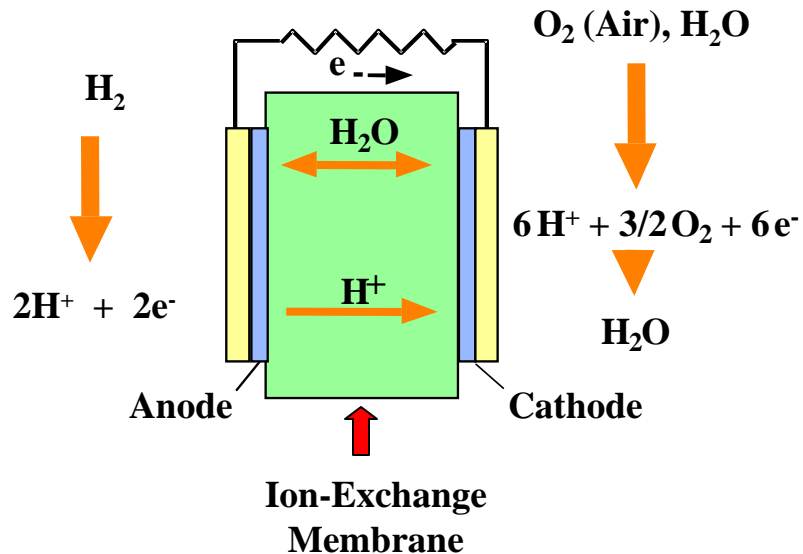
CASE SCHOOL OF ENGINEERING

Polymeric Membranes for Fuel Cells: Overview and Future Outlook

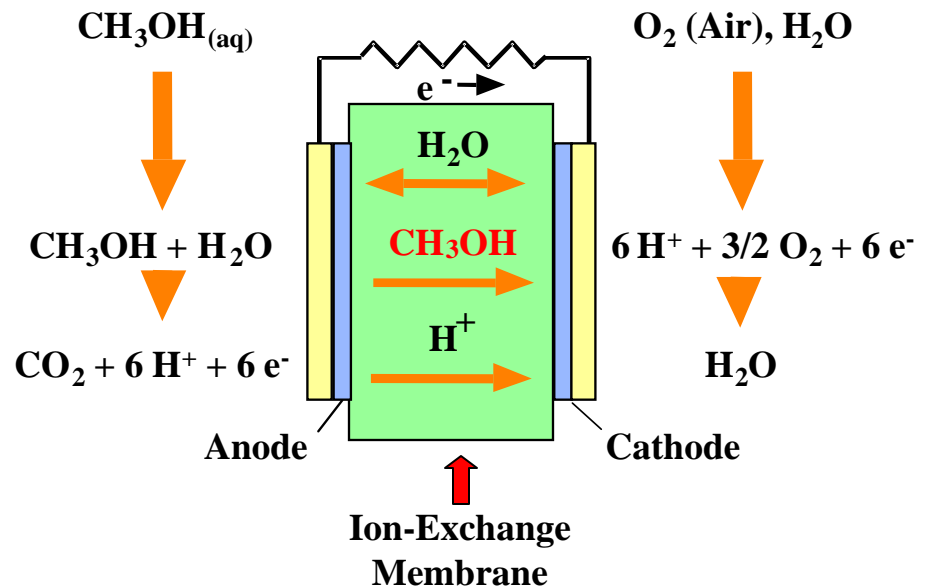
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Case Western Reserve University
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Proton-Exchange Membrane (PEM) Fuel Cells



Direct Methanol Fuel Cell (DFMC)



The Ion (Proton) Exchange Membrane in a Fuel Cell

Purpose:

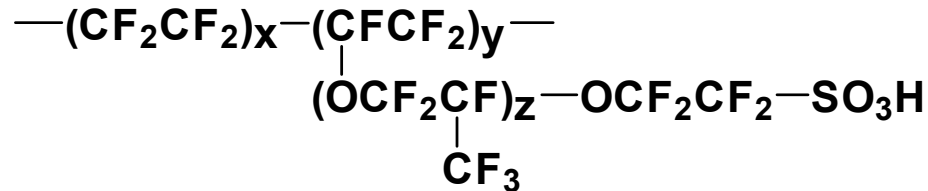
- To separate the anode and cathode
- To prevent mixing of the fuel and oxidant
- To provide a conductive pathway for protons

Required Properties:

- High ionic conductivity (and zero electronic conductivity) under cell operating conditions.
- Long-term chemical and mechanical stability at elevated temperatures in oxidizing and reducing environments.
- Good mechanical strength, with resistance to swelling.
- Low oxidant and fuel cross-over and pinhole free.
- Interfacial compatibility with catalyst layers.
- Low cost.

Challenges for Membrane Scientists and Engineers

PEM Material of Choice for H₂/Air Fuel Cell at 80°C is Nafion™



The Problems with Nafion: (i) Methanol diffusion is too high for a DMFC.
(ii) Nafion dehydrates at $T > 80^\circ\text{C}$ and $\text{RH} < 100\%$.
(iii) Expensive

What is Needed:

- *For a direct methanol fuel cell: A membrane with a high proton conductivity and low methanol crossover.*
- *For a H₂/Air Fuel Cell: A membrane with a high proton conductivity at $T \approx 120^\circ\text{C}$ and $\approx 25\% \text{ RH}$, or better, a membrane that operates without water at elevated T .*

Strategies for DMFC Membranes

DMFC Membrane Approach: Control water/methanol swelling and transport in an ion-exchange membrane by:

Modifying Nafion

Impregnation Nafion in an inert, hydrophobic support.

Use a crosslinkable polymer

Blending a sulfonated polymer with a hydrophobic polymer

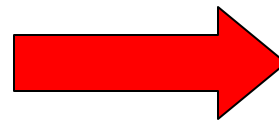
Use of block copolymers

The problem common to many ion-exchange membranes for DMFC

- *The decrease in methanol crossover comes at a price: a decrease in proton conductivity.*
 - *So, for proper fuel cell performance, thinner membranes (low sheet resistance), must be used, which negates the low methanol permeability.*

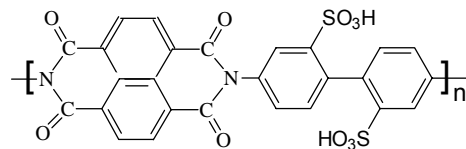
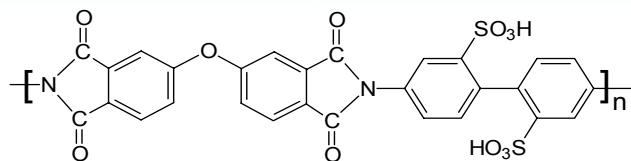
Modifications to Nafion (to reduce methanol crossover)

- Nafion/silica
- Nafion/zirconium phosphate
- Nafion/Pd
- Nafion/polyvinyl alcohol
- Nafion/montmorillonite
- Surface modification of Nafion
 - plasma etching
 - palladium sputtering
 - low dose EB
- Multilayer system
 - Nafion/Nafion-PVDF/Nafion

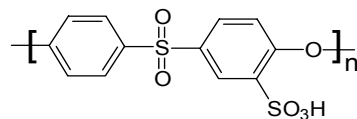
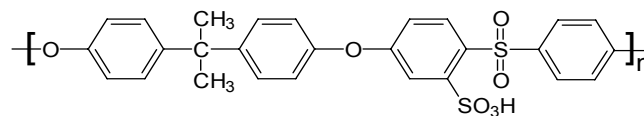
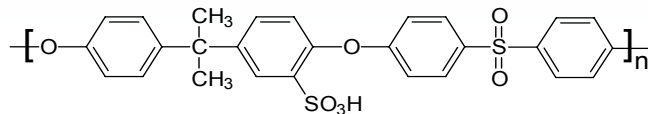


Results have not met expectations

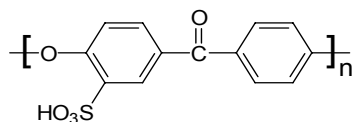
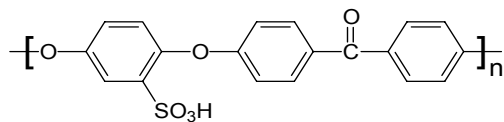
DMFC Membrane Selection – The Use of Aromatic Sulfonic Acid Polymers



POLYIMIDES

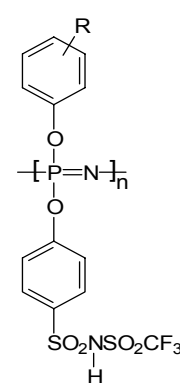
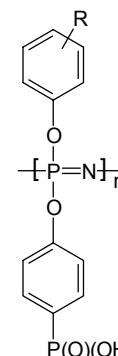
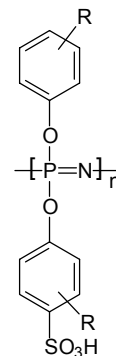


POLYSULFONES

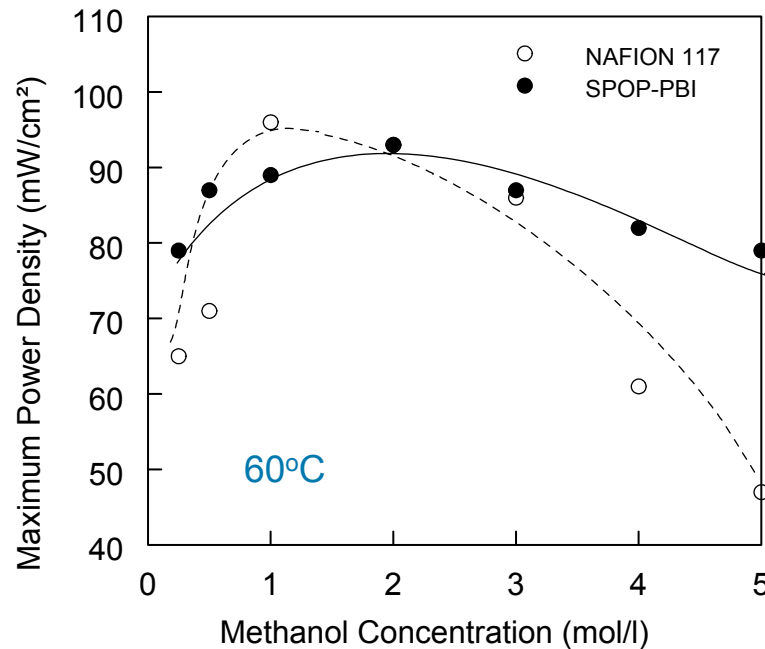
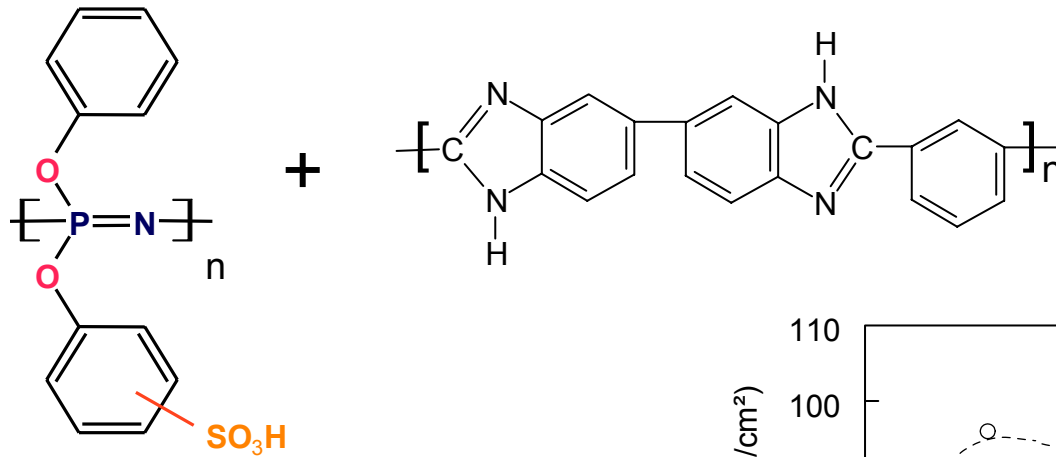


POLY(ETHER KETONES)

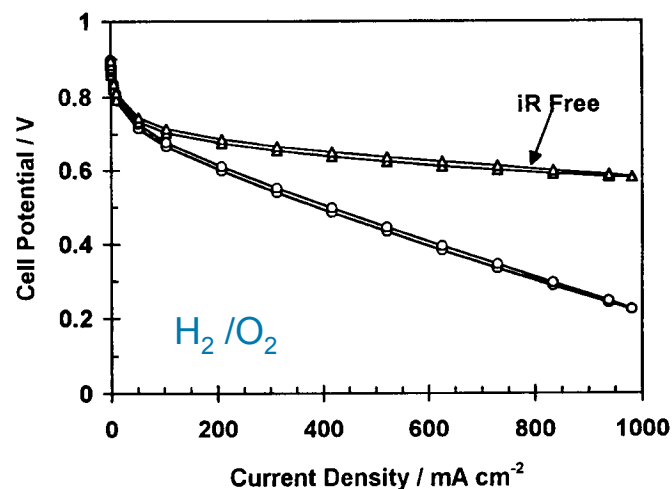
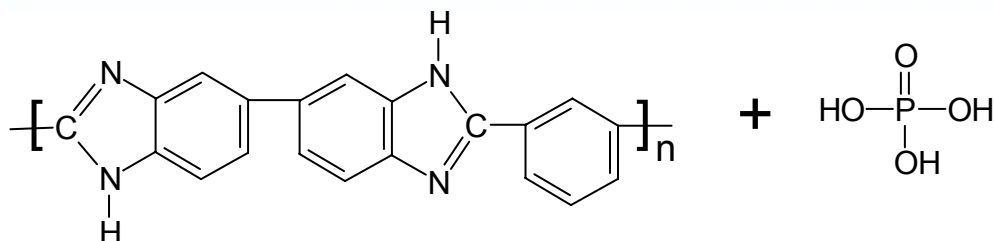
POLYPHOSPHAZENES



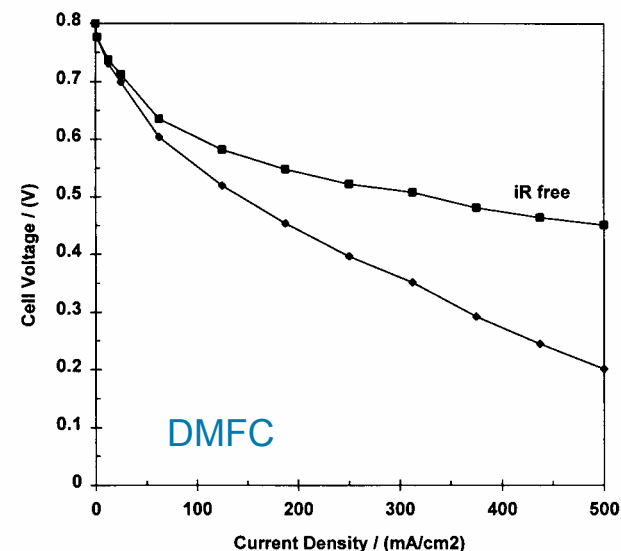
DMFC Results: Sulfonated Polyphosphazene-PBI Blends (Pintauro and Wycisk, CWRU)



Acid-Doped PBI for Direct Methanol and High Temp. H₂/air and Fuel Cells (Savinell and Litt, CWRU)



Hydrogen: 1 atm. humidified at 48°C and oxygen: 1 atm, humidified at 28°C. Cell resistance: 0.45 ohm. Cell operating temperature: 150°C.



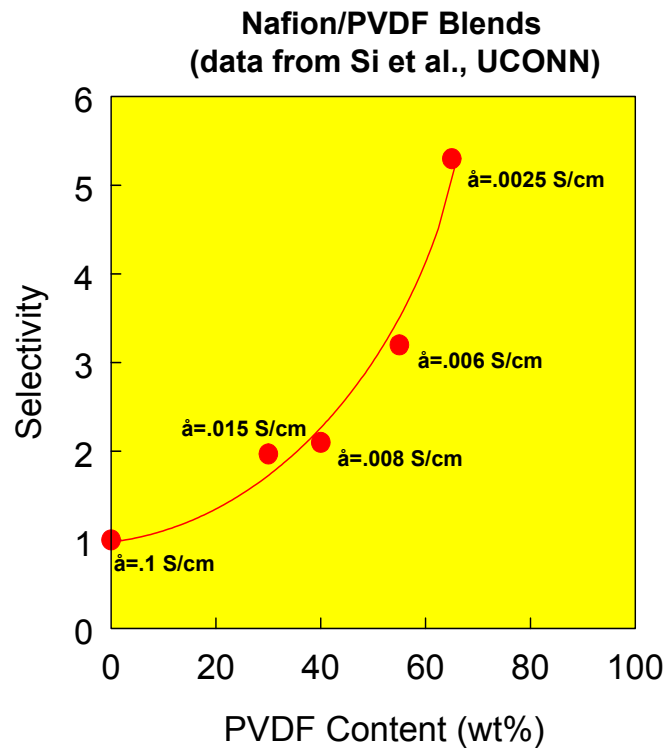
PBI/H₃PO₄ (480 m/o) membrane. Anode feed 4:1 H₂O/CH₃OH (by mole), temperature 200°C, P=1 atm. Membrane thickness 0.01 cm.

10-times lower methanol crossover, as compared to Nafion 117. But Problems:

- Must use methanol vapor for anode feed.
- There can be no liquid condensation.
- Oxygen reduction kinetics are slow.

Future Trends – Direct Methanol Fuel Cells

The ratio of proton conductivity (σ , S/cm) to methanol permeability (P , cm²/s) is the key selectivity parameter.

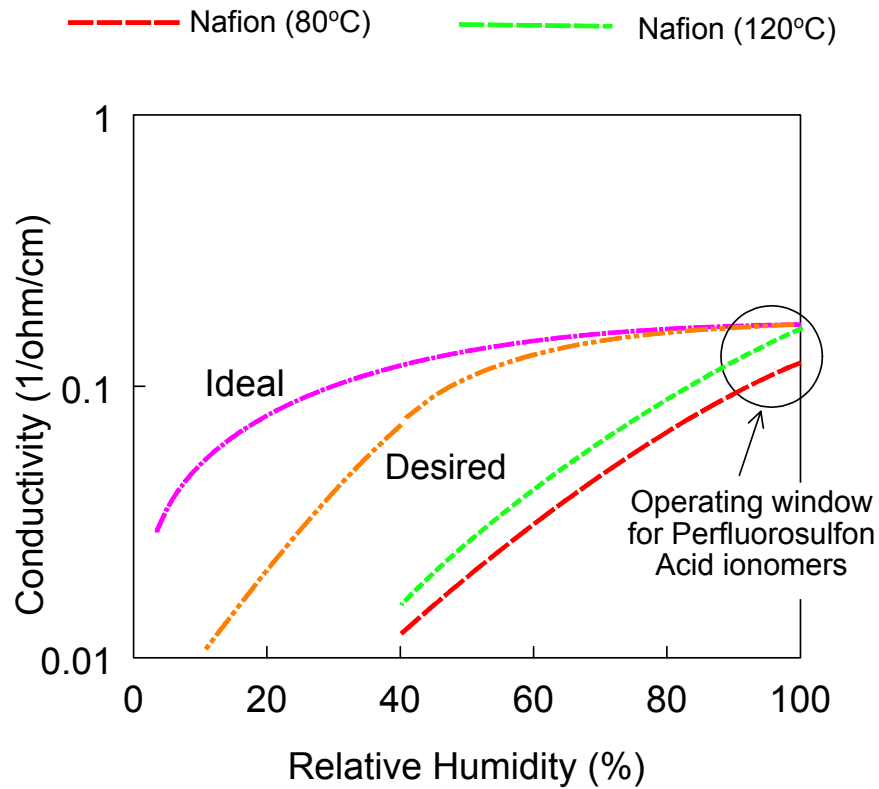


$$\text{Selectivity} = \frac{\left[\frac{\sigma}{P} \right]_{\text{MemX}}}{\left[\frac{\sigma}{P} \right]_{\text{Nafion}}}$$

- For some membranes, the selectivity increases as the membrane proton conductivity decreases.
- For high MeOH barrier membranes with acceptable sheet resistance (thickness/ σ), use very thin membranes ($< 10 \mu\text{m}$).
- *For such a thin, low conductivity membrane, how does one fabricate an MEA?*

High Temperature H_2 /air Fuel Cells: Nafion Dehydrates at High T

For $T > 100^\circ$: (1) Nafion dehydrates, with a loss in proton conductivity at RH < 100%



Strategies for High Temperature H₂/Air Fuel Cells

Modifications to Nafion

- *Addition of water-retaining (hydrophilic) additives*
 - *Non-conducting inorganic particles (SiO₂, TiO₂)*
 - *Proton conducting inorganic salts and heteropolyacids (e.g., zirconium phosphate/phosphonate and phosphotungstic acid)*

Substitution of water with a high boiling proton solvent (imidazole, benzimidazole)

- *If water boiled at 200°C, most of the problems related to PEM fuel cell operation at $T > 100^{\circ}\text{C}$ would be resolved.*

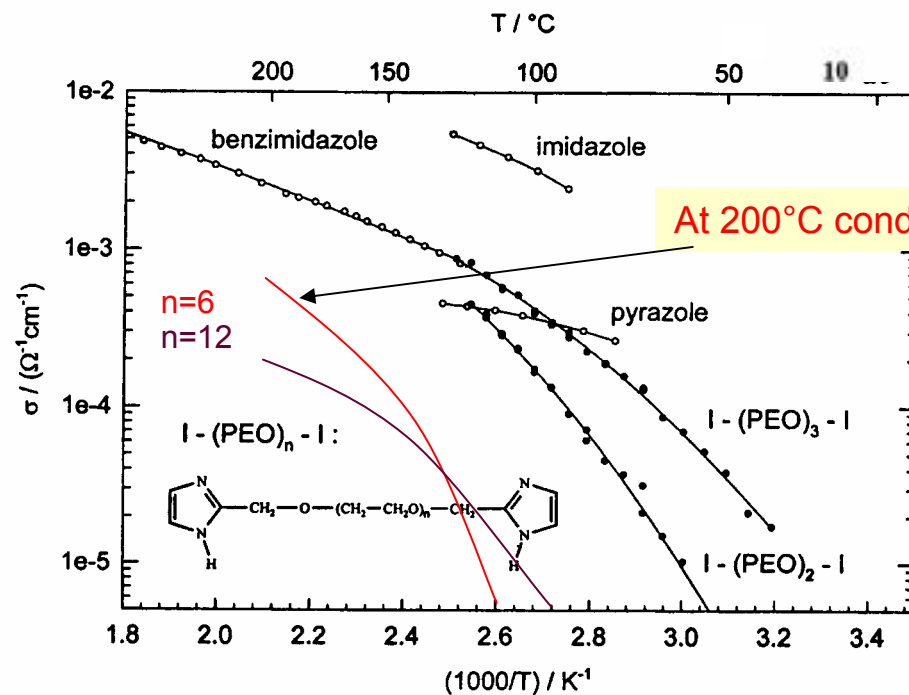
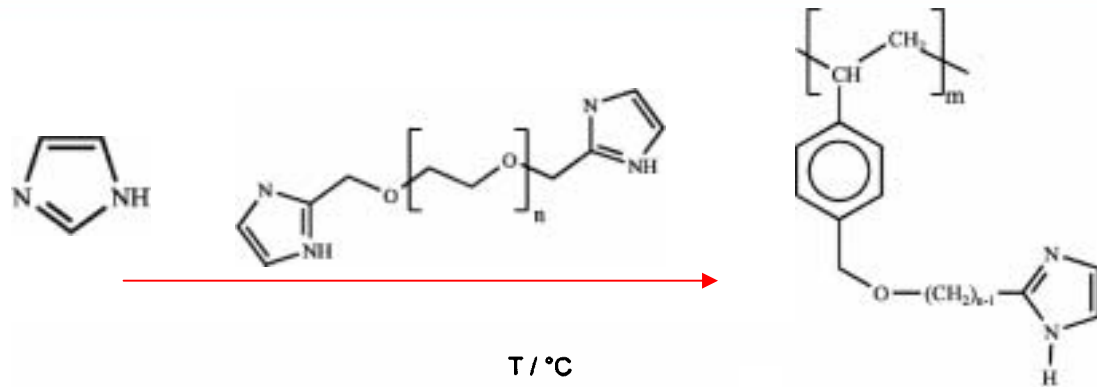
The problems with these approaches:

- *No significant improvement in proton conductivity at low humidity (water retention is not as good as expected and water is not where it is needed)*
- *Imidazolium groups are not as good as water in solvating membrane acid groups.*

High Temperature H₂/Air Fuel Cells: Eliminating Water as the Proton-Accepting Solvent (Kreuer et al.)

Two Approaches:

- Basic polymer with excess acid (PBI doped with concentrated phosphoric acid).
- Acidic polymer with excess base (sulfonated polymer with absorbed imidazole, benzimidazole or another appropriate proton acceptor).



Future Trends for High Temperature H₂/Air Fuel Cell Membranes

Eliminate the Need for Water in a Proton Exchange Membrane

Basic polymer with added excess acid (PBI doped with concentrated phosphoric acid)

Acidic polymer with added base (sulfonated polymer with absorbed imidazole, benzimidazole or some other proton acceptor).

Inorganic solid acids (bound in a polymeric matrix).

Hold Water in the Proton Exchange Membrane

Examine membranes with a highly uniform nano-pore structure. Utilize capillary condensation to hold water in membrane pores at $T > 100^\circ\text{C}$ and $\text{RH} < 100\%$. Use rigid or highly crosslinked polymers.

Desired proton conductivity: 0.1 S/cm at 120°C and 25% RH

Caveats:

- Aromatic sulfonic acids are unstable in the presence of water at $T > 100^\circ\text{C}$.
- Making a new membrane is not enough – one must make a membrane-electrode-assembly and test it in a fuel cell.

How Can X-Ray and Neutron Techniques be Used?

Understanding and manipulation of membrane micro-morphology is becoming increasingly important in the design/fabrication of fuel cell membranes.

- ***Can we adjust/control polymer morphology to create the desired properties?***

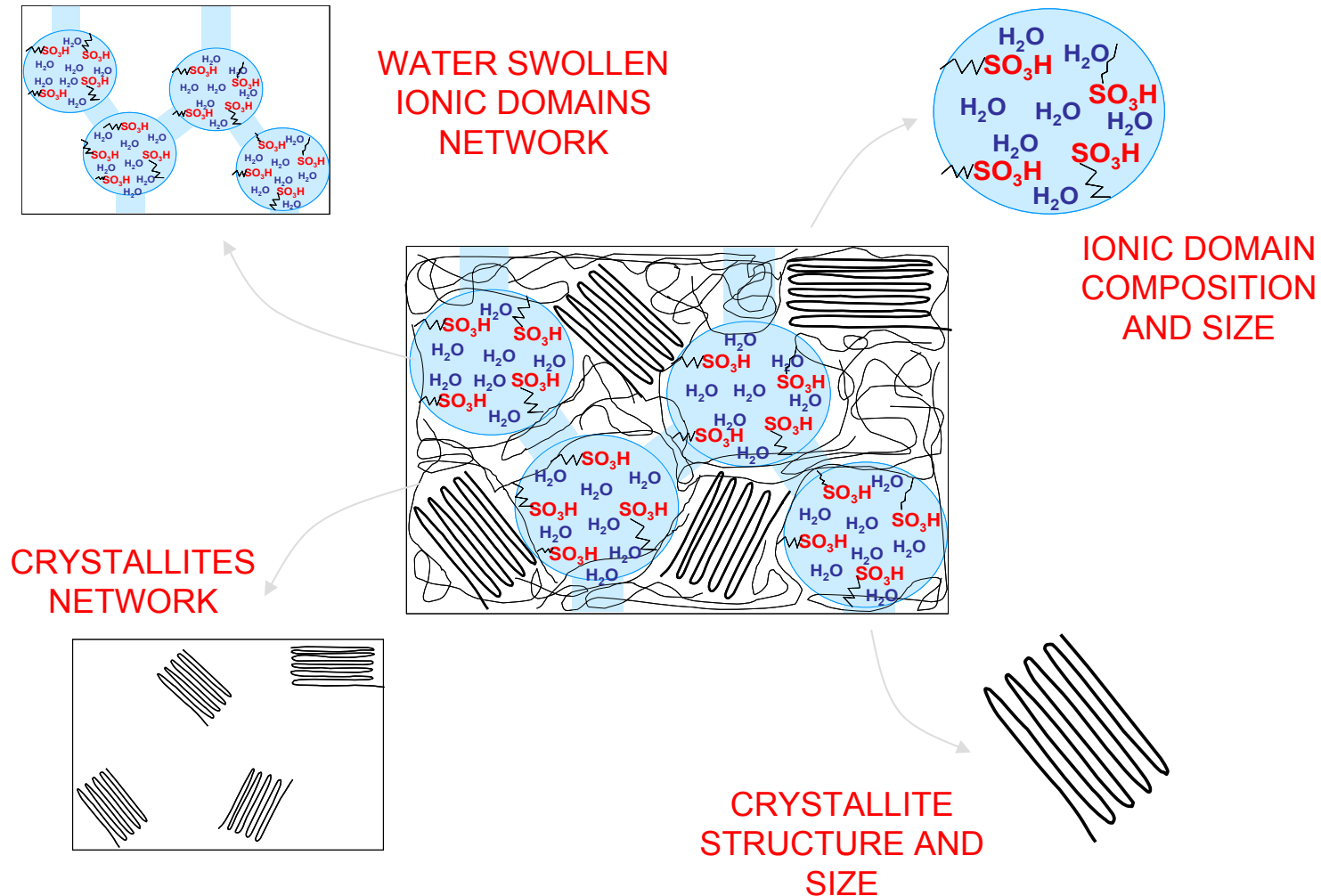
e.g., Nafion (with an ion-exchange capacity of 0.91 mmol/g) has a high proton conductivity due to ion-exchange group clustering (and a high acid strength).

Use WAXS, SAXS, and SANS to probe the micro-structure of fuel cell membranes.

Link the membrane micro-morphology to macroscopic membrane performance (proton conductivity, fuel permeability, swelling, and mechanical properties).

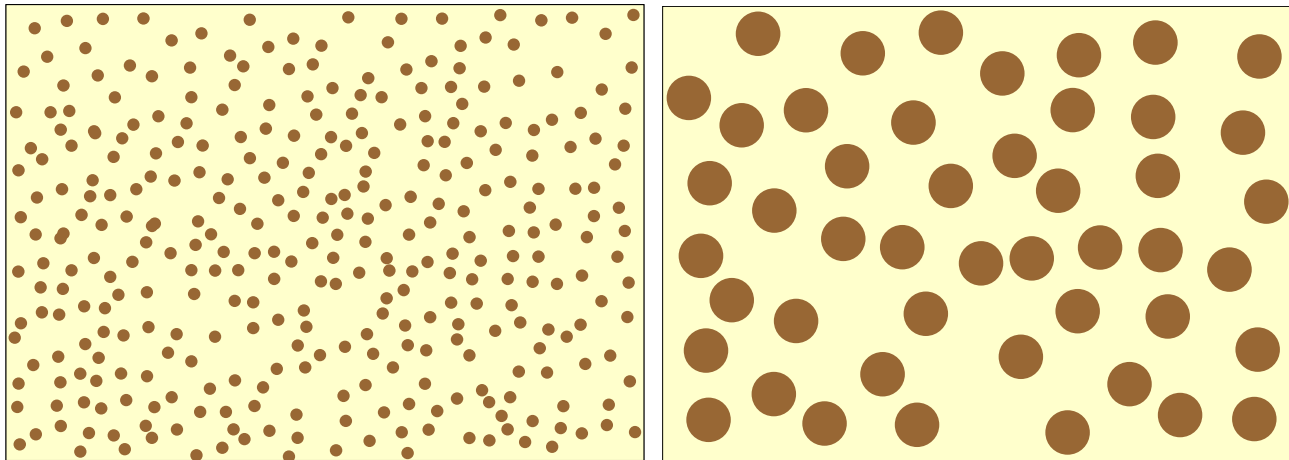
Design and fabricate better membranes.

Classical Copolymer Morphology (ionomeric domains in an inert semi-crystalline matrix) – Use X-Rays and/or Neutrons to Probe all Regimes



Micro-morphology: Domain-Size Effect in Blended Membranes (e.g., Nafion/PVDF blends)

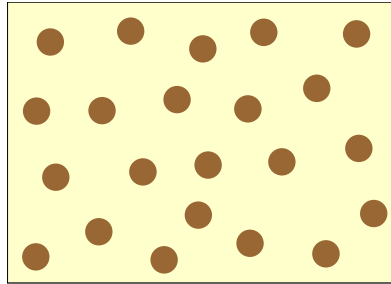
PROTOGENIC CLUSTERS (DOMAINS) DISPERSED
IN A NONCONDUCTING POLYMER MATRIX



FROM PERCOLATION THEORY:

CRITICAL VOLUME FRACTION IS SMALLER FOR SYSTEMS
WITH LARGER DOMAINS

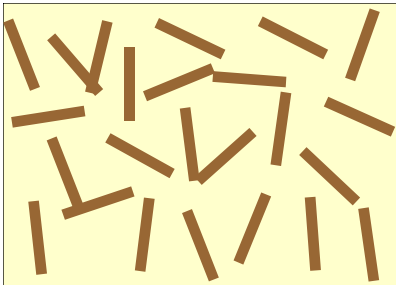
Micro-morphology: Nanocomposite Membranes (e.g., addition of silica or clay to a charged polymer)



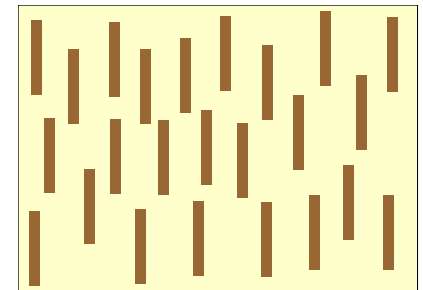
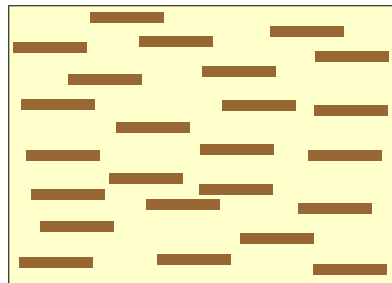
SPHERICAL DOMAINS OF
SILICATE COMPONENT
(e.g., via sol-gel condensation)

ORIENTATION OF CLAY PLATELETS: **RANDOM, HORIZONTAL, VERTICAL**

RANDOM ORIENTATION (GOOD FOR
SWELLING REDUCTION)

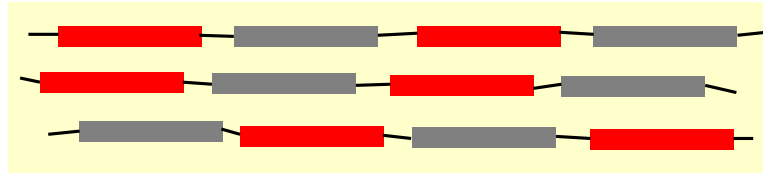


GOOD FOR BLOCKING METHANOL

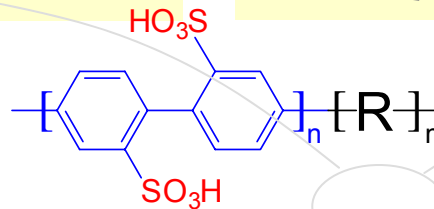
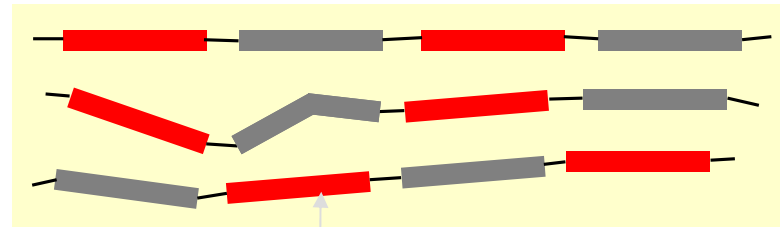
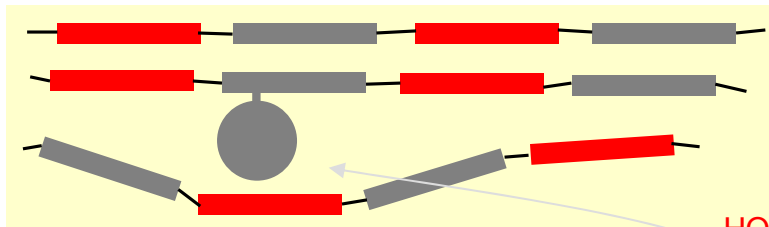


GOOD FOR PROTON CONDUCTIVITY (?)

Micro-morphology: Increasing Permanent Free Volume



POLYIMIDES OR POLYPHENYLENES (Litt et al., CWRU)



Membranes from rigid, liquid crystalline polymers, containing bulky or angled co-monomers, to create permanent pores (increase free volume).

Expected **improvement of water retention capability** for elevated temperature fuel cell operation (as compared to elastomeric polymers that readily swell and shrink).